

NaOH-Catalyzed Dimerization of Monofunctionalized Hydrofullerenes: Transition-Metal-Free, General, and Efficient Synthesis of Single-Bonded [60]Fullerene Dimers

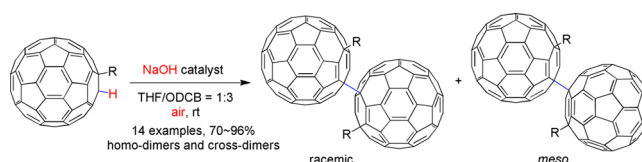
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Received May 24, 2012

ABSTRACT



Unprecedented, transition-metal-free NaOH-catalyzed homo- and cross-dimerizations of monofunctionalized hydrofullerenes are reported. Various single-bonded fullerene dimers were synthesized under mild reaction conditions with remarkably high yields. The use of a NaOH catalyst combined with tetrahydrofuran as a cosolvent under an air atmosphere is critical in achieving highly efficient catalytic dimerization.

The single-bonded fullerene dimer $\text{RC}_{60}\text{--C}_{60}\text{R}$ with a direct covalent bond between two C_{60} cages has attracted much attention due to not only its potential interesting optical and electronic properties through the interaction of two adjacent fullerene cages¹ but also its useful functionalization ability as a monomer radical (RC_{60}^\bullet) precursor.² The pioneered experimental and theoretical studies on these fullerene dimers revealed that they consist of racemic and *meso* isomers which were usually formed by the dimerization of RC_{60}^\bullet .^{3,4} Accordingly, in the past few

years, versatile synthetic methods for the construction of the single-bonded fullerene dimers have been reported.^{2–8} For example, the photoirradiation radical addition of C_{60} with perfluoroalkyl iodides in the presence of $(\text{R}_3\text{Sn})_2$,^{4a} $\text{Mn}(\text{OAc})_3$ -mediated radical reaction of C_{60} with phosphonate esters or dialkyl malonates,^{4c,6} one-electron oxidation of the monoanion RC_{60}^- through an excess amount of oxidants,^{2b,4b,5d,7} and electroreduction of 1,2-(PhCH_2)- HC_{60} ⁸ have been reported to form the single-bonded fullerene dimers. However, their wide application to the

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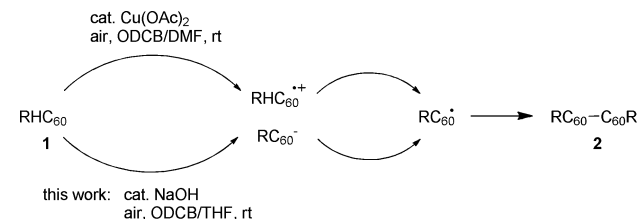
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elaborated fullerene dimers generally suffered from the limited scope of functional groups, low chemical yields, harsh reaction conditions, and use of large excess amounts of toxic reagents or additives. Recent advances in the catalytic functionalization of fullerene⁹ triggered us to explore the highly efficient catalytic dimerization of hydrofullerenes which may offer advantages such as high chemical yields and selectivity as well as high functional group compatibility under mild conditions.

Most recently, we found that the $\text{Cu}(\text{OAc})_2$ catalyst combined with a small amount of DMF as a cosolvent under air was crucial for dramatic enhancement of the dimerization efficiency of monosubstituted hydrofullerenes (RHC_{60}) (**1**),^{9m} affording the corresponding fullerene dimers **2** in high yields (Scheme 1).¹⁰ The reaction most probably proceeds through the $\text{Cu}(\text{OAc})_2$ -catalyzed generation of a fullerenyl radical cation species ($\text{RHC}_{60}^{\bullet+}$) followed by formation of a fullerenyl monoradical RC_{60}^{\bullet} . However, the drawback of toxic copper contamination of the products and solvents may preclude its use in materials science and practical synthetic application.¹¹ Taking these points into consideration, we envisioned that by using the suitable, nontoxic base as a catalyst in the presence of air and cosolvent, the catalytic dimerization of RHC_{60} (**1**) should be accomplished through the generation of mono-anion RC_{60}^- with base treatment followed by formation of RC_{60}^{\bullet} by one-electron oxidation.^{5d,12} Herein, we report unprecedented, efficient, and nontoxic NaOH-catalyzed homo- and cross-dimerizations of monofunctionalized hydrofullerenes **1** that afford the single-bonded fullerene dimers **2** as a mixture of racemic and *meso* isomers in excellent yields in the presence of air and tetrahydrofuran (THF) cosolvent under mild reaction conditions (Scheme 1). To the best of our knowledge, this is the first example for transition-metal-free catalytic functionalization of fullerenes which provides an alternative and promising method for catalytic dimerization of hydrofullerenes, meeting the requirements for both green chemistry and fullerene chemistry.

In the preliminary experiment, we found that the homo-dimerization of monosubstituted **1a** in the presence of an

Scheme 1. $\text{Cu}(\text{OAc})_2$ - and NaOH-Catalyzed Dimerization of Hydrofullerenes **1** for Synthesis of Single-Bonded [60]Fullerene Dimers **2**



as-prepared NaOH (10 mol %) by using ODCB (*ortho*-dichlorobenzene) as a sole solvent in air at rt did not proceed, and **1a** was recovered almost quantitatively (Table 1, entry 1). The remarkable enhancement of efficiency by adding DMF or CH_3CN , which was reported by our previous $\text{Cu}(\text{OAc})_2$ -catalyzed dimerization,¹⁰ led us to examine the notable cosolvent effect on the present dimerization. To our delight, addition of the polar cosolvents, such as DMF, THF, and CH_3CN , improved the yields of the corresponding dimer **2a** drastically to 89%, 95%, and 90%, respectively (entries 2–4), although we reported previously that the use of THF as a cosolvent combined with the $\text{Cu}(\text{OAc})_2$ catalyst afforded only a 20% yield of **2a**.¹⁰ Addition of less-coordinative cosolvents, such as toluene or chloroform, did not exert any influences on the reaction efficiency (entries 5 and 6). Previously, we also reported that the use of a catalytic or stoichiometric amount of $\text{Cu}(\text{OAc})_2$ in the absence of air produced the corresponding dimer **2a** in 14% and 93% yields, respectively.¹⁰ Interestingly, in sharp contrast to these results, the present NaOH-mediated dimerization did not afford the corresponding dimer **2a** with either a catalytic or stoichiometric amount of NaOH (entries 7 and 8). These results not only indicate that air play as an important role in the generation of monomer radical RC_{60}^{\bullet} but also imply that the present NaOH-catalyzed dimerization might form RC_{60}^{\bullet} in a completely different way from the $\text{Cu}(\text{OAc})_2$ -catalyzed reaction. To gain further insight into the role of bases, we examined various base catalysts. Strong inorganic bases, such as KOMe, KO^tBu, CsOH, and KOH, produced the corresponding fullerene dimer **2a** in high yields (entries 9–12), while other inorganic bases having a relatively lower basicity, such as LiOH and Na_2CO_3 , are less active (entries 13 and 14). Strong organic base Me₄NOH produced **2a** in a short reaction time (2 h), but the yield was lower than that of NaOH (entry 15). The weaker organic base Et₃N showed low catalytic activity regardless of the prolonged reaction time (entry 16). It is clear that the reaction did not proceed without base catalysts (entry 17).

With the optimized reaction conditions in hand, various monosubstituted hydrofullerenes **1** were examined as shown in Table 2. A variety of functional groups in hydrofullerenes **1** were tolerated under the present NaOH-catalyzed dimerization conditions, affording the corresponding single-bonded fullerene dimers **2** in very high

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1a: R = CC(=O)Oc1ccccc1C(=O)O

racemic

2a

meso

^a Conditions: To a 1,2-dichlorobenzene (ODCB) (3 mL) and cosolvent (1 mL) of **1a** (0.03 mmol) under air atmosphere was added base catalyst (10 mol %, 1 M aqueous solution). The resulting mixture was stirred at rt for the times shown. ^b HPLC yields determined using C₆₀ as an internal standard. Isolated yield by silica-gel chromatography is shown in parentheses. ^c Reaction was conducted under argon atmosphere. ^d 1.0 equiv of NaOH catalyst was used. ^e A THF solution was used.

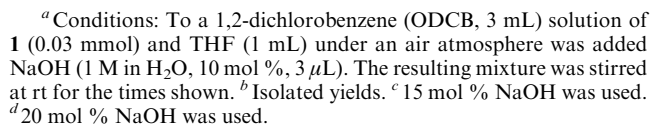
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The reaction scheme shows the dimerization of a C₆₀ derivative (1) under the following conditions: NaOH (10 mol %), THF/DCB = 1/3, air, rt. The product is a mixture of a racemic dimer (2) and a meso dimer (3).

Structure 1: A C₆₀ cage with an R group and an H atom at adjacent positions.

Structure 2 (racemic): A dimer of two C₆₀ cages where the R groups are in a trans configuration.

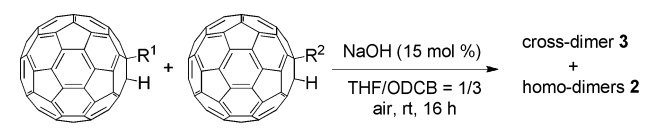
Structure 3 (meso): A dimer of two C₆₀ cages where the R groups are in a cis configuration.



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solution. It should be noted that both homo- and cross-dimers are very stable in the solid state; they can be stored for several months at ambient temperature without any decomposition.

Table 3. NaOH-Catalyzed Cross-Dimerization^a



| entry | 1 (R ¹) | 1 (R ²) | homodimer 2 (%) ^b | cross-dimer 3 (%) ^b |
|-------|---------------------|---------------------|------------------------------------|--------------------------------|
| 1 | 1a | 1g | 24 (2a); 29 (2g) | 30 (3a) |
| 2 | 1a | 1f | 26 (2a); 28 (2f) | 34 (3b) |
| 3 | 1f | 1g | 29 (2f); 29 (2g) | 33 (3c) |

^a Conditions: To a 1,2-dichlorobenzene (ODCB, 6 mL) solution of two different hydrofullerenes **1** (0.03 mmol) and THF (2 mL) under an air atmosphere was added NaOH (15 mol %, 1 M aqueous solution). The resulting mixture was stirred at rt for 16 h. ^b Dimers **2** and **3** were isolated by silica-gel chromatography.

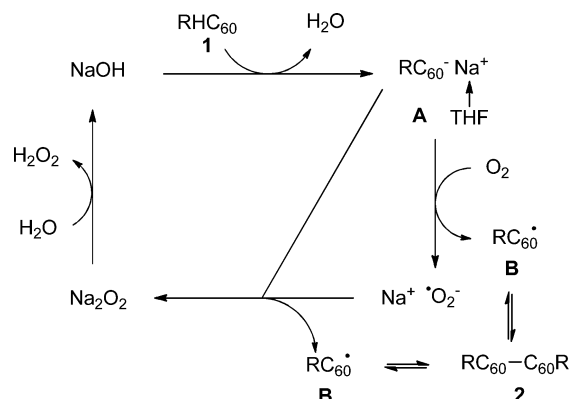
A notable feature of an acidic C–H bond¹³ in hydrofullerenes **1** and our experimental observations, as well as early works on base catalyzed dimerization of mercaptans,¹² led us to propose the monoanion oxidation mechanism as shown in Scheme 2.¹⁴ Initially, deprotonation of an acidic proton in hydrofullerenes **1** by the strong base NaOH forms a fullereryl monoanion sodium complex **A**, wherein a polar solvent such as THF may stabilize **A**. Indeed, when hydrofullerene **1a** was treated with a stoichiometric amount of NaOH in an argon atmosphere without air, the color of the reaction mixture was changed to dark green, indicating the generation of a monoanion species (Table 1, entry 8).^{4b} One-electron oxidation of the monoanion sodium complex **A** by O₂ in air forms the monoradical **B** which produces the corresponding single-bonded fullerene dimers **2**.^{4b,5b,5d,12} Moreover, we assume that further one-electron oxidation of monoanion **A** may take place by an *in situ* generated [•]O₂[–] oxidant, leading to monoradical **B**.^{12a} Finally, hydrolysis of sodium peroxide regenerates the NaOH catalyst which enters into the next catalytic circle. Dimerization of two monoradicals having an *R* and *S* configuration produces the *meso* isomer (*R*-*S*),

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(14) An alternative reaction pathway, such as the generation of a fullerenol intermediate through hydroxylation of **1a**, is unlikely because, without any fullerenol, derivatives were observed from ¹H NMR and HPLC analysis under the standard reaction conditions and the reaction using H₂O₂ instead of air; the reaction of **1a** under aqueous basic conditions in the presence of H₂O₂ (50 equiv) in an argon atmosphere produced the corresponding dimer **2a** in 23% yield (8 h) together with a 72% yield of the recovered **1a**.

whereas dimerization of two monoradicals with the same configuration gives a racemic mixture of *R*-*R* and *S*-*S* isomers.^{4c}

Scheme 2. A Plausible Mechanism for the NaOH-Catalyzed Dimerization of Monosubstituted Hydrofullerenes



In conclusion, we have developed unprecedented, transition-metal-free NaOH-catalyzed homo- and cross-dimerizations of monofunctionalized hydrofullerenes. The present novel catalytic dimerization provided a general, efficient, mild, and green method for the construction of various single-bonded fullerene dimers with remarkably high yields. Compared with our previous Cu(OAc)₂-catalyzed dimerization, the present NaOH catalysis avoided use of the toxic and expensive copper salts while retaining its high catalytic efficiency. The NaOH catalyst combined with a small amount of THF as a cosolvent in air is crucial for the efficient formation of the corresponding single-bonded fullerene dimers. Investigation on their chemical and electronic properties and application to materials science are in progress.

Acknowledgment. This work was partially supported by World Premier International Research Center Initiative (WPI), MEXT (Japan). T.J. acknowledges a Grant-in-Aid for Scientific Research on Innovative Areas “Organic Synthesis Based on Reaction Integration. Development of New Methods and Creation of New Substances” from the MEXT (Japan). S.L. acknowledges the support of the JSPS fellowships for Young Scientists.

Supporting Information Available. Experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.